ESRF	**Experiment title:** Solid state reactions at nanoscale: In-situ and real time study of the silicide formation, nanostructuration, and interfacial roughness by combined X-ray diffraction, X-ray reflectivity, sheet resistance and reflectometry laser	**Experiment number**: **MA331**
Beamline: BM05	**Date of experiment**: from: 13 July 2010 to: 19 July 2010	**Date of report**: 30 July 2010
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THIS REPORT IS A PRELIMINARY AND INTERMEDIARY REPORT ON THE FINAL LTP MA331 REPORT THAT WILL BE SUBMITTED IN JANUARY 2011.

1. Introduction

1.1 Sum-up of the technical and scientific milestones and work carried out

During the Long Term Project (LTP) MA331, we developed a new experimental setup allowing to combine three in-situ (during heat treatment) and real time characterization techniques (x-ray diffraction (XRD), x-ray reflectivity (XRR), and sheet resistance measurements (Rs)) in order to study the silicide formation kinetics and stability. Two of these techniques require a powerful and stable x-ray source because of the small amount of matter that is analyzed and the requested surface sensitivity.

This set-up is composed by a vacuum chamber, equipped with a furnace and a 4 point probes system to measure the sheet resistance. Kapton windows are positionned on the vacuum chamber to allow simultaneous XRD and XRR measurements.

To achieve this experimental set-up, we have:

- improved the in-situ fast XRR measurement using the older BM05 furnace and vertical diffractometer;
- determined the experimental conditions allowing simultaneously XRR and XRD measurements on the BM05 beamline and on our samples;
- completed the new vacuum chamber that allows simultaneously XRD, XRR, and Rs measurements;
- developed a software and implemented an algorithm to analyze the XRR data by Fast Fourier Transform;
- overcame the mechanical issues to mount the new chamber on the BM05 horizontal diffractometer;
- completed the use of the new chamber on the BM05 horizontal diffractometer and optimized the simultaneous XRR, XRD and Rs data acquisition in collaboration with the ESRF bliss staff and the BM05 staff.

1.2 State of the experimental set-up and use

⇨ The set-up is now working (see final LTP report that will be submitted January 2011) and nice results were obtained on Ni-silicide system, and especially on Ni(13%Pt)/Si(100) by both XRD and XRR in-situ measurements [1].

Even if this experimental set-up was built to study the silicide formation kinetics, it can be used more generally for the study of solid state reactions at nanoscale: actually it allows measuring in-situ (during sample annealling) and simultaneously:

- x-ray diffraction patterns to study the structural changes of the layer,
- x-ray reflectivity to follow the layer thickness, density and roughness evolutions (even if the layer is amorphous),
- sheet resistance to obtain the change in electrical properties of the layer.

⇨ Thus, any change in one of these parameters can be observed during thin layer annealing. If this (these) change(s) is(are) due to a phase formation or to a phase transition, then this phenomena can be studied using the three characterization techniques (XRD, RRX and Rs) simultaneously.

1.3 Test experiment on other systems

⇨ During the last MA331 LTP experiments (12-19 jully 2010), we used the last 3 shifts to test our set-up on $Ge_2Sb_2Te_5$ (GST) thin films.

GST is a chalcogenide system belonging to the family of the pseudobinary alloys of GeTe and Sb_2Te_3. The solid GST phases are a stable hexagonal and two metastable phases (the amorphous and the polycrystalline face centered cubic (fcc)). The latter two are characterized by a very large variation of the optical (low and high reflectivity for amorphous and crystalline states respectively) and electrical properties (high and low resistivity for amorphous and crystalline phases respectively). The amorphous-to-*fcc* phase transition can be reversibly induced by laser illumination or current pulses. For these reasons, these materials have been used as optical rewritable storage media and have also been more recently proposed for phase change nonvolatile random access memories (PCRAM) [2,3,4]. The storage mechanism is based on a reversible phase change between amorphous and crystalline states. In PCRAM solid state memories, the two logic states are represented by the crystalline (low resistivity) and amorphous (high resistivity) states.

The mechanisms of the GST crystallization are not yet fully understood and are usually studied by in-situ XRD (see e.g. [5]), in-situ optical transmission or reflection (with visible light wavelength) (see e.g. [6]), and in-situ sheet resistance (see e.g. [7]). It has to be stressed that these techniques are generally used separately. Ex-situ (after deposition) x-ray reflectivity was also used to characterize GST layer [8]; however, to our knowledge, neither in-situ x-ray reflectivity nor combined and simultaneous XRR, XRD and Rs in-situ measurements was used to study the GST crystallization mechanisms.

2. Experimental method

$Ge_2Sb_2Te_5$ thin films with thickness ranging from 15 to 150 nm were deposited by RF magnetron sputtering (using an alloy target) at IM2NP on 200 nm SiO_2/Si(100) substrates. In situ XRR, XRD and Rs measurements were performed on the BM05 horizontal diffractometer with constant heating rates (2°C/min) up to 315°C, using the IM2NP vacuum chamber equipped with a furnace and a four point probes sheet resistance set-up. The vacuum measured in the chamber was at least 1×10^{-6} mbar. A thermocouple was used to control the temperature of the heating element and another one was in contact with the surface of the sample. For XRR measurements, we used the zapscan movements that enable recording in most cases an accurate XRR pattern with a counting time of 60s-70s. XRD was measured at a fixed angle using the IM2NP Andor camera, and a picture was taken every 70s. As the GST layers have a very high resistivity, the R_S measurement was not optimized because of the current supplier. However, we managed to record the sheet resistance value every 70s. The multilayer monochromators of BM05 was positioned to work at a fixed energy of 12keV, in order to record both XRR and XRD patterns in an appropriate 2θ range.

3. Results

35 nm thick $Ge_2Sb_2Te_5$ layer deposited on 200nm SiO_2/Si(100) substrate was used to test the experimental protocol. XRR, XRD and Rs data were simultaneously recorded while annealing the sample at a constant heating rate (2°C/min) up to 315°C.

Figure 1 shows XRR patterns measured in situ during heating. Whatever the temperature, the well marked fringes indicate that the layer roughness remains low. XRR patterns are very similar up to 150°C where a clear change is observed. The fringe angular positions and the critical angle for total reflection change abruptly. These features indicate a significant modification of the density and thickness of GST layer. Above 170°C, XRR patterns do not exhibit drastic changes characteristic of a stable phase.

Figure 2a shows the inverse fast Fourier transform (IFFT) of the XRR patterns. It thus represents the evolution of the distance between the interfaces of the sample stack versus the annealing time. As our sample is composed by one layer, the IFFT figure exhibits one peak around 35 nm. In accordance with the XRR pattern evolution, this peak remains unchanged below 150°C, and above 170°C. In between a clear shift appears: the layer thickness decreases from about 35nm to about 31nm.

To analyze more precisely the layer density and thickness variation, two XRR patterns measured at room temperature and 315°C were fitted. Experimental and simulated curves are shown in Figure 2b. The parameters introduced to adjust the simulated curves show that the shift in the XRR spectra corresponds to a layer density increase of 7 %, and to a layer thickness decrease of 7.6 %.

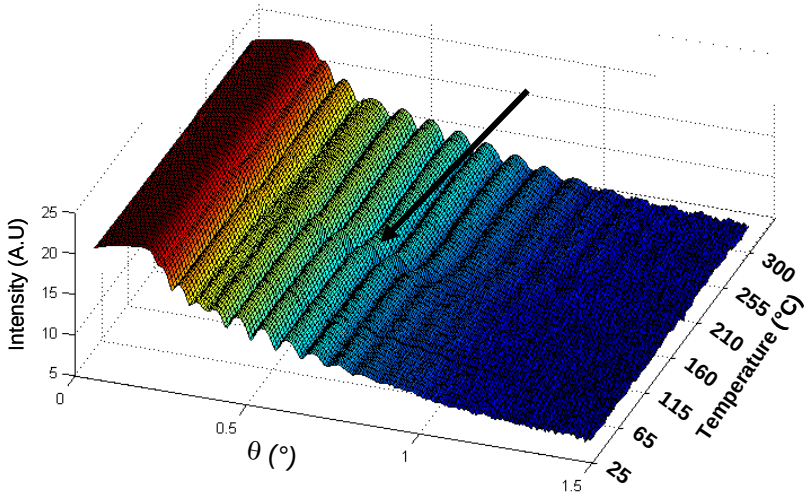
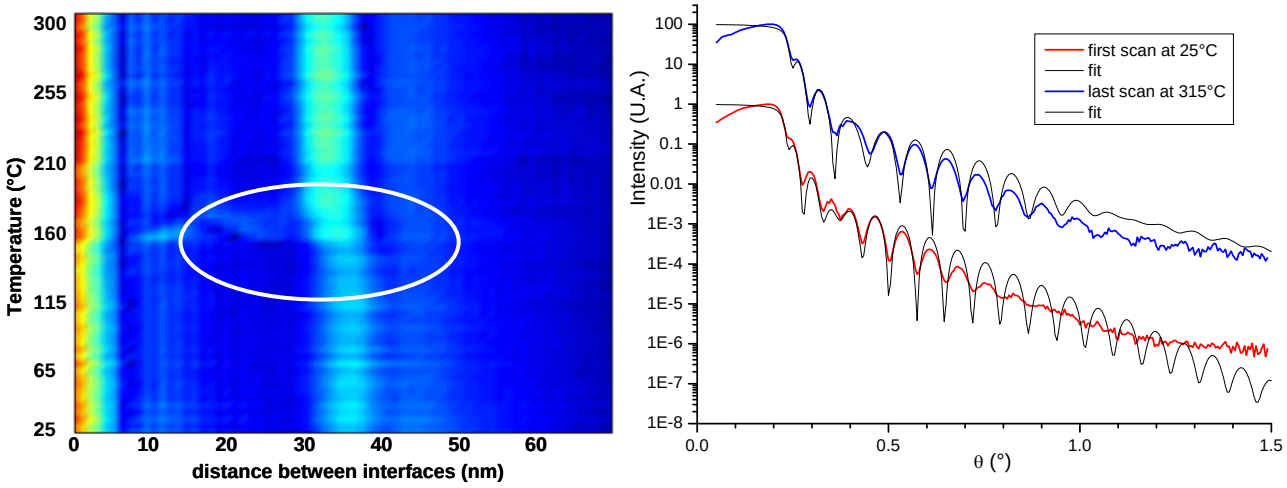


Figure 1 : XRR patterns recorded on 35 nm GST/SiO_2 during an anneal at constant rate (2°C/min) (λ = 1.035 Å)



(a) **(b)**

Figure 2: Analysis of XRR patterns: (a) IFFT curves of the XRR patterns of Figure1; each horizontal line corresponds to the IFFT of one XRR curve. (b) Experimental and simulated XRR curves at room temperature (red) and at 315°C (blue); the intensity of the curve at 315°C is multiplied by 100.

Figure 3 shows the in-situ XRD diagrams recorded simultaneously with the XRR data of Figure 1. At room temperature, no diffraction peak is detectable, indicating that the layer is amorphous in agreement with conventional XRD experiments performed at IM2NP after the deposition. As the temperature increases, two diffraction peaks appear

around 160°C. Both diffraction lines may be indexed in cubic symmetry corresponding to the fcc $Ge_2Sb_2Te_5$ crystalline phase.

Finally, Figure 4 shows the in-situ resistivity measurement performed on the same sample during XRR and XRD pattern acquisition. Concomitantly with modifications observed on XRR and XRD patterns, the resistivity falls around 160°C. The decrease of several orders of magnitude indicates that the GST film undergoes a transition from high resistance state to a low resistance state.

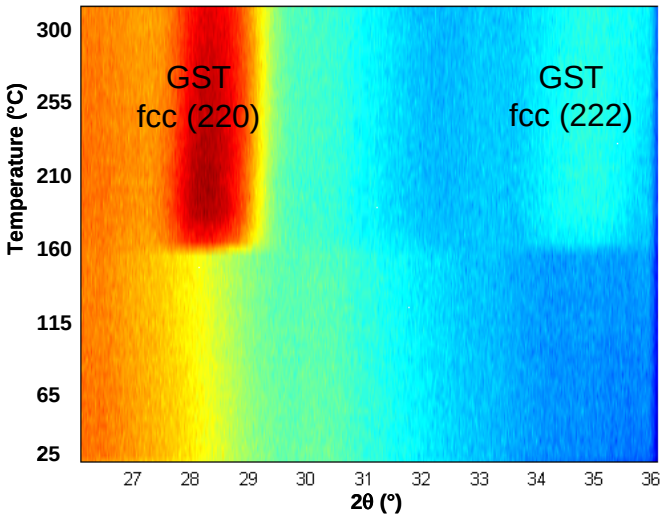


Figure 3: In-situ XRD diagrams recorded simultaneously with XRR patterns presented in Figure 1 (λ = 1.035 Å, constant rate 2°C/min) on the same sample (35 nm GST/SiO_2)

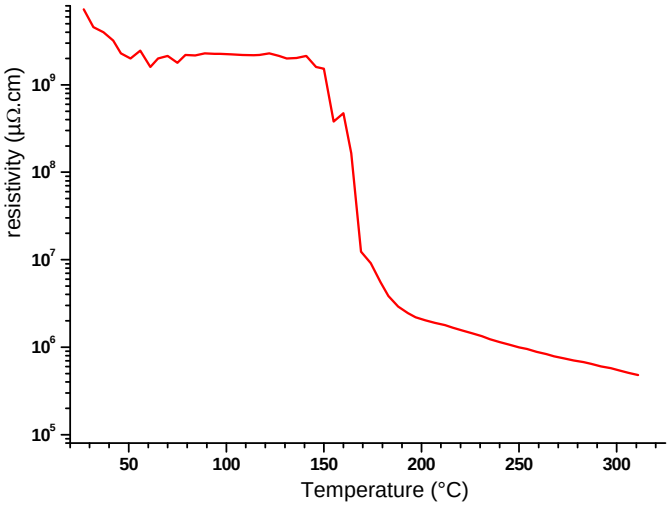


Figure 4: In-situ electrical resistivity recorded simultaneously during XRR and XRD data acquisition (constant rate 2°C/min) on the same sample (35 nm GST/SiO_2).

To sum-up, simultaneous XRR, XRD and Rs in situ measurements are consistent since they clearly show concomitant electrical and structural changes when GST layer undergoes the amorphous-to-crystalline phase transition. By comparing Figure 2a, Figure 3 and Figure 4 we can conclude that the crystallization temperature is in the range 150 – 160°C: this comparison is made on Figure 5 where the data extracted from the three in-situ experiments are plotted. The GST layer crystallizes in a cubic symmetry corresponding to the standard fcc structure. Further XRD investigations are in progress at the IM2NP lab, using conventional x-ray diffraction to check the presence of other crystalline phases.

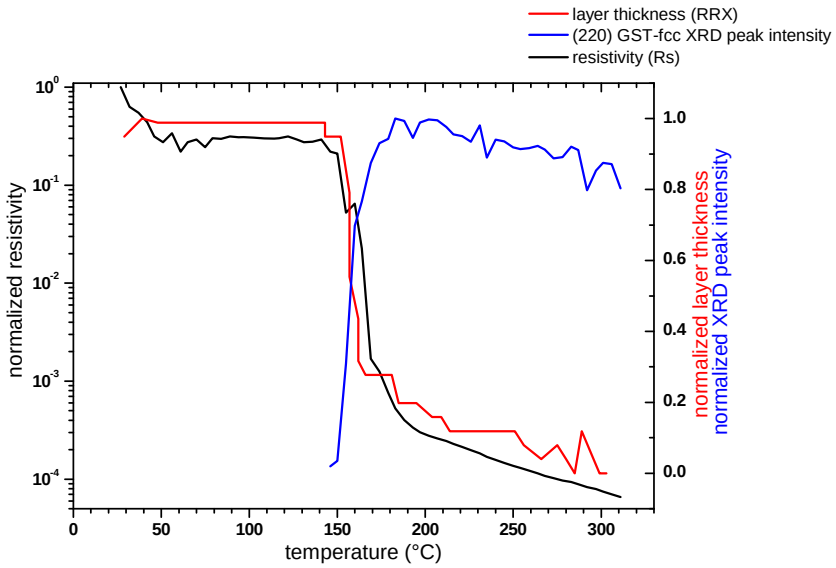


Figure 5: comparison of the data obtained by the simulatenous XRR (layer thickness), XRD (peak intensity) and Rs experiment (resistivity) versus the temperature.

Moreover, the in-situ XRR experiment coupled with IFFT analysis enables determining the temperature-dependent evolution of the GST layer thickness. Contrary to other techniques such as XRD, the layer thickness can be directly calculated without any physical assumption (if the layer density is homogeneous, if not, no XRR signal will be obtained).

⇨ The recorded data are now under analysis and a paper on these first results is in preparation.

4. Conclusion

During the MA331 LTP we developed a new experimental setup that enables combing in-situ and real time characterization techniques, *i.e.* x-ray diffraction (XRD), x-ray reflectivity (XRR), and sheet resistance measurements (Rs). Besides, we also developed a computer code to analyze the XRR data in "real time" (*i.e.* during or just after the measurement) by Fast Fourier Transform (FFT) algorithm. This allows to directly testing the XRR measurement quality after each in-situ experiment.

Although the experimental setup was mainly dedicated to the silicide formation kinetics, 3 shifts of the last MA331 LTP experiment were devoted to the amorphous-to-crystalline phase transition in GST thin film. The high quality results demonstrate the relevance of such an experimental protocol enabling direct correlations between electrical and microstructural changes. These experiments enabled (i) determining the temperature crystallization and the symmetry of crystallized phase from XRD; (ii) studying the time-dependent evolution of GST film thickness, roughness and density from XRR; and (iii) measuring conductivity change during amorphous-to-crystalline transition from sheet resistance.

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